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(54) **Electronic coating materials using mixed polymers**

(57) The present invention provides a method of forming coatings on electronic substrates and claims the substrates coated thereby. Our method comprises ap-

plying a coating comprising hydrogen silsesquioxane resin and a polysilazane on a substrate and then heating the coated substrate at a temperature sufficient to convert the resins to ceramics.

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Description

The present invention relates to a method of forming coatings on electronic substrates using mixtures of hydrogen silsesquioxane resin (H-resin) and polysilazanes. These combinations provide coatings with unique properties and characteristics.

The use of H-resin derived ceramic coatings on substrates such as electronic devices is known in the art. For instance, US-A 4,756,977 discloses a process for forming a silica coating on an electronic substrate wherein a solution of H-resin is applied to a substrate followed by heating the coated substrate in air at a temperature in the range of 200-1000°C. This patent, however, does not describe using a mixture of resins to form the coating.

Similarly, the use of polysilazanes to form ceramic coatings on electronic devices is known in the art. For example, WO 93/02472 and US-A 5,358,739 teach processes for forming coatings on electronic substrates wherein polysilazane resins are applied to electronic substrates followed by heating the coated substrates to convert the polysilazanes into ceramics. These publications also do not describe using a mixture of polymers.

We have now found that useful coatings can be formed from mixtures of H-resin and polysilazanes.

The present invention provides a method of forming a coating on an electronic substrate and claims the substrates coated thereby. The method comprises first applying a composition comprising between 10 and 90 wt% H-resin and between 90 and 10 wt% polysilazane on the substrate. The coated substrate is then heated at a temperature sufficient to convert the composition to a ceramic coating.

The present invention also introduces the coating composition comprising between 10 and 90 wt% H-resin and between 90 and 10 wt% polysilazane diluted in a solvent which is used to form various types of coatings.

The present invention is based on our finding that desirable coatings are formed from a composition comprising H-resin and a polysilazane. Coatings derived therefrom can be thicker (e.g., > 1 micrometer) than those derived from H-resin alone and they can also be crack and pore-free.

Because of these advantages, our coatings are particularly valuable on electronic substrates. Such coatings can serve, for example, as protective coatings, dielectric coatings, interlevel dielectric layers and the like.

As used herein, the expression "ceramic coating" describes the hard coating obtained after heating the hydrogen silsesquioxane and polysilazane mixture. This coating contains amorphous silica (SiO_2) materials as well as amorphous silica-like materials that are not fully free of residual carbon, silanol (Si-OH), nitrogen (Si-N) and/or hydrogen. The expression "electronic substrate" is meant to include, but is not limited to, electronic devices or electronic circuits such as silicon based devices, gallium arsenide based devices, focal plane arrays,

opto-electronic devices, photovoltaic cells and optical devices.

In the process of this invention, a ceramic coating is formed on an electronic substrate by a process which comprises applying a coating composition comprising H-resin and a polysilazane onto the substrate and then heating the coated substrate at a temperature sufficient to convert the composition to a ceramic.

The H-resins which may be used in this invention include hydridosiloxane resins of the formula $\text{HSi}(\text{OH})_x(\text{OR})_y\text{O}_{z/2}$, in which each R is independently an organic group or a substituted organic group which, when bonded to silicon through the oxygen atom, forms a hydrolyzable substituent, $x = 0-2$, $y = 0-2$, $z = 1-3$, $x + y + z = 3$. Examples of R include alkyls such as methyl, ethyl, propyl and butyl; aryls such as phenyl; and alkenyls such as allyl or vinyl. As such, these resins may be fully condensed ($\text{HSiO}_{3/2}$)_n or they may be only partially hydrolyzed (i.e., containing some Si-OR) and/or partially condensed (i.e., containing some Si-OH). Although not represented by this structure, these resins may contain a small number (e.g., less than 10%) of silicon atoms which have either 0 or 2 hydrogen atoms attached thereto due to various factors involved in their formation or handling.

The above H-resins and methods for their production are known in the art. For example, US-A 3,615,272, teaches the production of a nearly fully condensed H-resin (which may contain up to 100-300 ppm silanol) by a process comprising hydrolyzing trichlorosilane in a hydrolysis medium of benzenesulfonic acid hydrate and then washing the resultant resin with water or aqueous sulfuric acid. Similarly, US-A 5,010,159 provides an alternative method comprising hydrolyzing hydridosilanes in a hydrolysis medium of arylsulfonic acid hydrate to form a resin which is then contacted with a neutralizing agent.

Other hydridosiloxane resins, such as those described by US-A 4,999,397; those described in JP-As 59-178749, 60-86017 and 63-107122; or any other equivalent hydridosiloxane, will also function herein.

The polysilazanes (or silazane polymers) useful in this invention are generally well known in the art and their structure is not particularly critical. The polysilazanes of this invention generally contain units of the type $[\text{R}_2\text{SiNH}]$, $[\text{RSi}(\text{NH})_{3/2}]$ and/or $[\text{R}_3\text{Si}(\text{NH})_{1/2}]$ wherein each R is independently selected from the group consisting of hydrogen atom, alkyl radicals containing 1 to 20 carbon atoms, aryl radicals and alkenyl radicals. Naturally, the polysilazanes useful in this invention may contain other silazane units. Examples of such units include $[\text{MeSi}(\text{NH})_{3/2}]$, $[\text{Me}_2\text{SiNH}]$, $[\text{ViSi}(\text{NH})_{3/2}]$, $[\text{Vi}_2\text{SiNH}]$, $[\text{PhMeSiNH}]$, $[\text{PhViSiNH}]$, $[\text{MeViSiNH}]$, $[\text{HSi}(\text{NH})_{3/2}]$ and $[\text{H}_2\text{SiNH}]$. Mixtures of polysilazanes may also be employed in the practice of our invention.

The polysilazanes of this invention are prepared by techniques well known in the art. The actual method used to prepare the polysilazane is not critical. Suitable

silazane polymers or polysilazanes may be prepared by the methods of US-As 4,540,803 and 4,543,344. Other suitable polysilazanes can be prepared by the methods of US-As 4,312,970, 4,340,619, 4,395,460, 4,404,153, 4,482,689, 4,397,828, 4,543,344, 4,656,300, 4,689,252 and 5,030,744. Still other polysilazanes include those of EP-As 0 351 747 and 0 332 374.

Especially preferred polysilazanes are those which have no carbon in the polymer repeating units since the resultant coatings will have little carbon contamination. End blocking groups such as $\text{Me}_3\text{Si}(\text{NH})_{1/2}$ are acceptable in such polymers since they are generally removed during the subsequent pyrolysis.

The most preferred polymers used herein are those of US-As 4,340,619 and 4,540,803. The silazane polymers of the former patent are prepared by contacting and reacting in an inert, essentially anhydrous atmosphere a chlorine containing disilane or mixture of chlorine containing disilanes of the general formula $(\text{Cl}_x\text{R}_y\text{Si})_2$ with a disilazane having the general formula $(\text{R}_3\text{Si})_2\text{NH}$ at a temperature in the range of 25°C. to 300°C. while distilling volatile byproducts, wherein R is vinyl, an alkyl group of 1-3 carbon atoms or a phenyl group; R' is vinyl, hydrogen atom, an alkyl group of 1-3 carbon atoms or a phenyl group; x has a value of 0.5-3; y has a value of 0-2.5 and the sum of x+y is 3. An especially preferred embodiment therein involves the reaction of methylchlorodisilanes with hexamethyldisilazane to produce methylpolydisilylazane. The product silazane polymers of US-A 4,340,619 may have a relatively high chloride ion content and it is preferred that such concentration be lowered before use in our invention. A method for such removal is more fully described in US-A 4,772,516 which comprises treating the polymer with ammonia for a time sufficient to remove the chlorine.

The silazane polymers of US-A 4,540,803 are prepared by a method which comprises contacting and reacting in an inert essentially anhydrous atmosphere, trichlorosilane with a disilazane at a temperature in the range of 25°C. to 300°C. while distilling volatile byproducts. The disilazane used in the process has the formula $(\text{R}_3\text{Si})_2\text{NH}$ where R is selected from the group consisting of vinyl, phenyl and alkyl radicals containing 1 to 3 carbon atoms or hydrogen atom. An especially preferred embodiment of this latter patent involves the reaction of trichlorosilane with hexamethyldisilazane to produce hydridopolysilazane.

In addition, polysilazanes doped with boron (i.e., polyborosilazanes or borosilazanes) are also usable within the present invention and are included in our definition of polysilazanes. These borosilazanes are also generally well known in the art and their structure is not particularly critical. The boron content of these polymers is likewise generally not crucial and, thus, can vary over a wide range (eg., 0.1-50 wt %). Generally, the backbone of the borosilazanes of this invention contain Si-B, Si-N and B-N bonds with the remaining valences of

these atoms filled by groups independently selected from the group consisting of hydrogen atom; alkyl radicals containing 1 to 20 carbon atoms such as methyl, ethyl and propyl; aryl radicals such as phenyl; and alkenyl radicals such as vinyl. Preferred borosilazanes are those in which there is no carbon in the repeating units of the polymer, i.e., there may be carbon in the polymeric endcaps.

Examples of specific borosilazanes include, for instance, those described by Seyferth et al., J. Am. Ceram. Soc. 73, 2131-2133 (1990) or Noth, B. Anorg. Chem. Org. Chem., 16(9), 618-21, (1961); those described in US-As 4,910,173, 5,169,908, 4,482,689, 5,030,744 and 4,604,367; or those described by EPAs 0 424 082 and 0 364 323.

The method for preparing such compounds is likewise known in the art and are described in the above references. Examples of such methods, however, typically comprise (1) reacting a boron trihalide with a silazane oligomer such as $(\text{RSi}(\text{NH})_{1.5})_x$ or $((\text{CH}_3)_3\text{Si})_2\text{NH}$, wherein R is selected from the group consisting of hydrogen atom, a hydrocarbon radical or a substituted hydrocarbon radical and x is an integer of 2-20; (2) reacting an organoborazine with an organopolysilane; and (3) the reaction of a boron compound such as a borane complex, boroxine, boron alkoxides and borazines with a polysilazane.

A particularly preferred polymer comprises the boron modified hydropolysilazane polymers of US-A 5,169,908. These polymers are produced by reacting a hydrosilazane polymer with a borane complex or diborane. In a more preferred embodiment of that patent, the hydropolysilazane is specifically produced by the reaction of trichlorosilane and hexamethyldisilazane as described in US-A 4,540,803.

If desired, other materials can also be added to our coating mixture. For instance, the claimed coating composition may contain a platinum, rhodium or copper catalyst to increase the rate and extent of conversion of the resins to silica. Generally, any platinum, rhodium or copper compound or complex thereof which can be solubilized will be functional. For instance, a composition such as platinum acetylacetonate, rhodium catalyst $\text{RhCl}_3[\text{S}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2]_3$, obtained from Dow Corning Corporation, Midland, Mich., or cupric naphthenate. These catalysts are generally added in an amount of between 5 to 1000 ppm platinum, rhodium or copper based on the weight of combined resins (H-resin and polysilazane).

It is also feasible to add particulate fillers to our mixture of resins. These include, for example, various inorganic and organic fillers, especially inorganic fillers, in a variety of morphologies including, but not limited to powders, particles, flakes, microballoons and filaments. Examples of inorganic fillers include synthetic and natural materials such as the oxides, nitrides, borides and carbides of various metals or non-metals such as glass, alumina, silica, silicon monoxide, zirconium oxide, tita-

nium dioxide, tantalum oxide, niobium oxide, zinc oxide, tungsten oxide, ruthenium oxide, silicon nitride, aluminum nitride, titanium diboride, silicon carbide, boron carbide and boron nitride; calcium carbonate; carbon, graphite, high dielectric constant fillers (eg >12) such as the titanate, niobate or tungstate salts of metals such as strontium, zirconium, barium, lead, lanthanum, iron, zinc and magnesium including, for example, barium titanate, potassium titanate, lead niobate, lithium titanate, strontium titanate, barium strontium titanate, lead lanthanum zirconium titanate, lead zirconium titanate and lead tungstate; radiopaque materials (materials which prevent penetration by radiation) such as the insoluble salts of barium, lead, silver, gold, cadmium, antimony, tin, palladium, strontium, tungsten and bismuth including, for example, salts such as carbonates, sulfates and oxides (e.g., barium sulfate); optically opaque fillers such as organic and inorganic pigments, silicon nitride powder, silicon carbide powder, aluminum nitride powder, silica and alumina; tamperproof materials (materials which render heat on oxidation) such as magnesium, iron, tin, silicon and zinc; magnetic materials such as carbon alloys, ferrites, iron carbonyls and alloys of metals such as iron, manganese, cobalt, nickel, copper, titanium, tungsten, vanadium, molybdenum, magnesium, aluminum, chromium, zirconium, lead, silicon and zinc including, for example, Fe_2O_3 , MnZn , NiZn , CuZn and other ferrite materials; metals which produce thermally or electrically conductive coatings such as gold, silver, copper, aluminum, nickel, zinc, chromium, cobalt and the like; phosphors and the like. Also, some organic materials such as cellulose, polyamides, aramid, phenol resins and the like may be used.

The amount of any filler used in the present invention can be varied over a wide range. Generally, however, the fillers are used in an amount less than 90 volume percent to insure that enough resin is present to bind the filler. Obviously, smaller amounts of fillers (eg., 1-5 wt%) can also be used.

Still other materials which may be present in our coating composition include, for example, agents which modify the surface of the filler for better adhesion or suspending agents. The adhesion promoters can include, for example, silanes such as glycidoxypolytrimethoxysilane, mercaptopropyltrimethoxysilane and vinyltriacetoxy silane. Generally, these are used in amounts of 0.1 to 5 wt%. The suspending agents can include, for example, cellulose, clay, fumed silica, stearates and the like. These are used in amounts sufficient to suspend any fillers (e.g., 1-25 wt%). These and other optional components are known to those skilled in the art.

According to the process of our invention, the H-resin, polysilazane and any optional components are applied to the surface of a substrate. This is accomplished in any manner, but a preferred method involves dissolving or dispersing the H-resin, polysilazane and any optional components in a solvent. This mixture is then applied to the surface of the substrate. Various fa-

cilitating measures such as stirring and/or heating may be then used to dissolve or disperse the materials and to create a more uniform application material. Solvents which may be used include any agent or mixture of agents which will dissolve or disperse the H-resin and polysilazane to form a homogenous liquid mixture without affecting the resultant coating. These solvents include, for example, aromatic hydrocarbons such as benzene or toluene, alkanes such as n-heptane or dodecane, ketones, esters, glycol ethers or cyclic dimethylpolysiloxanes, in an amount sufficient to dissolve/disperse the above materials to the concentration desired for application. Generally, enough of the above solvent is used to form a 0.1-80 weight percent mixture of the resins, preferably 1-50 wt%.

This mixture is then coated onto the substrate by spin coating, dip coating, spray coating or flow coating. Other equivalent means, however, are also deemed to be within the scope of this invention.

The solvent is then allowed to evaporate from the coated substrate resulting in the deposition of the a coating. Any suitable means of evaporation may be used such as simple air drying by exposure to an ambient environment, by the application of a vacuum or mild heat (e.g., less than 50°C.) or during the early stages of the heat treatment. It is noted that when spin coating is used, the additional drying period is minimized as the spinning drives off the solvent.

Although the above described methods primarily focus on using a liquid approach, one skilled in the art will recognize that other equivalent means can also function herein and are within the scope of this invention.

The coating is then typically converted to ceramic by heating it to a sufficient temperature. Generally, the temperature is in the range of 50 to 1000°C. depending on the pyrolysis atmosphere. Preferred temperatures are in the range of 50 to 800°C. and more preferably 50-500°C. Heating is generally conducted for a time sufficient to ceramify, generally up to 6 hours, with less than 3 hours being preferred.

The above heating may be conducted at any effective atmospheric pressure from vacuum to superatmospheric and under any effective oxidizing or non-oxidizing gaseous environment such as air, O_2 , ozone, an inert gas (N_2 , etc.), ammonia, amines, moisture, N_2O and H_2 .

Any method of heating such as the use of a convection oven, rapid thermal processing, hot plate or radiant or microwave energy is generally functional herein. The rate of heating, moreover, is also not critical, but it is most practical and preferred to heat as rapidly as possible.

By the above methods a ceramic coating is produced on the substrate. The thickness of the coating is generally greater than 0.5 micrometers and often greater than 1 micrometer. These coatings smooth the irregular surfaces of various substrates; they are relatively defect free; and they have excellent adhesive properties. As such, they are particularly useful for a variety of

electronic applications such as dielectric or protective layers and conductive layers.

Additional coatings may be applied over these coatings if desired. These include, for example, SiO₂ coatings. SiO₂/ceramic oxide layers, silicon containing coatings, silicon carbon containing coatings, silicon nitrogen containing coatings, silicon oxygen nitrogen coatings, silicon nitrogen carbon containing coatings and/or diamond like carbon coatings. Methods for the application of such coatings are known in the art and many are described in US-A 4,756,977. An especially preferred coating is silicon carbide applied by the chemical vapor deposition of silacyclobutane or trimethylsilane. This process is more completely described in US-A 5,011,706.

The following non-limiting examples are included so that one skilled in the art may more readily understand the invention.

Example 1

Hydrogen silsesquioxane resin, 0.9 g, produced by the method of US-A 3,615,272, 0.2 g of hydridopolysilazane (55.6 wt% solids in xylene) made by the method of US-A 4,540,803 and 60 ppm of Pt (from 0.1 g of platinum acetylacetonate) were mixed in 8.8 g of cyclic polydimethylsiloxanes. A 2.54 cm² silicon wafer was then spin coated with this solution at 3000 rpm for 20 seconds. The coating was pyrolyzed for 3 hours at 400°C. in air. FTIR spectra of the coating showed that the coating was essentially converted to silica. The coating thickness was 0.5086 micrometers and the refractive index was 1.442 (8300 lambda).

Example 2

Hydrogen silsesquioxane resin, 0.5 g, produced by the former method above, 1.0 g of hydridopolysilazane (55.6 wt% solids in xylene) made by the latter method above, 3.0 g of plasma alumina microballoons (6 micrometer) and 0.4 g of glycidoxypolytrimethoxysilane were mixed in 1 g cyclic polydimethylsiloxanes with a sonic probe to form a coating solution. An 11.25 cm² alumina panel was coated with the solution by using a 75 micrometer drawdown bar. The coated panel was air dried for 3 hours and 25 minutes and subsequently pyrolyzed for 1 hour at 400°C. in air. The pyrolyzed coating was examined with a microscope and found to have no cracks at 1000x magnification. The coating thickness was 48.7 micrometers.

Claims

1. A method of forming a coating on an electronic substrate comprising applying a coating composition comprising between 10 and 90 wt% hydrogen silsesquioxane resin and between 90 and 10 wt%

polysilazane onto an electronic substrate; and heating the coated substrate at a temperature sufficient to convert the coating composition into a ceramic coating.

2. The method of claim 1 wherein the coated substrate is heated at a temperature in the range of between 50°C. and 1000°C.
3. The method of claim 1 wherein the coated substrate is heated in an environment containing a gas selected from the group consisting of air, O₂, oxygen plasma, an inert gas, ammonia, amines, moisture, H₂ and N₂O.
4. The method of claim 1 wherein the coating composition also contains a platinum, rhodium or copper catalyst in an amount of between 5 and 500 ppm of platinum, rhodium or copper based on the weight of hydrogen silsesquioxane resin and polysilazane.
5. The method of claim 1 wherein the coating composition also contains a filler.
6. The method of claim 5 wherein the coating composition also contains a material which modifies the surface of the filler for better adhesion.
7. The method of claim 5 wherein the filler is selected from the group consisting of powders, particles, flakes, filaments and microballoons.
8. A coating composition comprising hydrogen silsesquioxane resin and a polysilazane diluted to between 0.1 and 80 wt% solids in a solvent, wherein the hydrogen silsesquioxane resin and polysilazane are present in a weight ratio of between 9:1 and 1:9.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 4296

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 466 205 A (DOW CORNING) 15 January 1992 * column 2, line 48 - column 14, line 18; claims 1-5 *	1-4,8	H01L21/316 C04B35/622 C04B41/87 H01L23/29 H01L21/56
A	EP 0 615 000 A (DOW CORNING) 14 September 1994 * page 2, line 22 - page 4, line 50; claims 1-18 *	1-8	
D,A	US 5 358 739 A (BANEY RONALD H ET AL) 25 October 1994 * column 1, line 45 - column 5, line 60; claims 1-9; table 1 *	1-3,8	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01L C04B
Place of search THE HAGUE		Date of completion of the search 4 March 1997	Examiner Königstein, C
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